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# Draft Assessment of Potential Treatment Technologies to Reduce Ion Loadings to Biologically-Impaired Streams with Ionic Stressors in the Lower Guyandotte River Watershed of WV

September 12, 2022

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PRESENTED TO

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**TETRA TECH**

EXECUTIVE SUMMARY

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(To be updated once report text is finalized)

DRAFT

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## ACRONYMS/ABBREVIATIONS

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Acronyms/Abbreviations	Definition
BCR	Biochemical reactor
CESR	Cost-Effective Sulfate Removal
EDR	Electrodialysis reversal
EPA	United States Environmental Protection Agency
FRA	Forest Reclamation Approach
mg/l	Milligrams per liter
µS/cm	microsiemens per centimeter
NF	nanofiltration
OSMRE	Office of Surface Mining Reclamation and Enforcement
RM	River mile
RO	Reverse osmosis
SC	Specific conductance
SMCRA	Surface Mining Control Reclamation Act
TDS	Total dissolved solids
TMDL	Total maximum daily load
TSS	Total suspended solids
USGS	United States Geological Survey
WV	West Virginia
WVDEP	West Virginia Department of Environmental Protection

## 1.0 EXECUTIVE SUMMARY

To be updated once report text is finalized

## 2.0 INTRODUCTION

Under contract with U.S. Environmental Protection Agency, Region 3 (EPA) and in consultation with the West Virginia Department of Environmental Protection (WVDEP), Tetra Tech is modeling ion constituents in biologically impaired streams of the Lower Guyandotte Watershed in West Virginia. The work is associated with streams experiencing elevated water column ionic strength that is contributing to nonattainment of the applicable narrative water quality criterion for biological integrity.

The work in this pilot project includes the development of a restoration target for water column specific conductance that, if attained, would substantively mitigate ionic stress to biota. The work also includes 1) dynamic modeling of existing conditions for key individual ions and specific conductance in targeted streams, and 2) the development of allocation scenarios with pollutant reductions to watershed point and nonpoint sources that will achieve the restoration target. The work does not include final total maximum daily load (TMDL) development but is expected to support future TMDL development, NPDES permitting and/or water quality standard variances in the Lower Guyandotte Watershed. Additionally, it is anticipated that this work will become the foundation for management actions to address ionic toxicity similar scenarios across West Virginia.

With respect to the restoration target, EPA and WVDEP have agreed on a long-term average water column specific conductance of approximately 400 microsiemens per centimeter ( $\mu\text{S}/\text{cm}$ ). For consistency with effluent limitation development in NPDES permitting, a maximum 4 consecutive day average target equal to 721  $\mu\text{S}/\text{cm}$  has also been derived. This maximum 4-day target of 721  $\mu\text{S}/\text{cm}$  corresponds to an annual average of 400  $\mu\text{S}/\text{cm}$ . Water column specific conductance observations greater than the targets have been documented in all the impaired streams included in this project. Baseline specific conductance varies by impaired stream, but many instream observations fall in the 1,500-2,000  $\mu\text{S}/\text{cm}$  range with higher discharge values expected. Under many scenarios, existing discharge values will need to be reduced to the allocation endpoint because of the lack of dilution in the receiving stream at the discharge location.

In recognition of the significant ion reductions that are needed, the novelty of application of ion reduction treatment in the mining industry, and the likely high cost and complexity of necessary controls, WVDEP and EPA are contemplating the pursuit of available water quality standard modifications that would allow extended time for restoration. As such, management controls that make incremental progress toward the endpoint are relevant, as are design considerations for new sources.

The purpose of this supporting memorandum is to summarize information about treatment technologies that are potentially available to reduce ionic loading from existing sources, with a focus on cost and the ability to achieve anticipated allocations. Additional considerations are provided with respect to land and energy requirements and the relative intensity of necessary operation and maintenance requirements.

Commented [AJ1]: Also include a statement about the 10% MOS and 649 target.

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## 3.0 BACKGROUND

### 3.1 ION SOURCES

Multiple sources of elevated ions exist within the watersheds of the impaired streams associated with this pilot project. The most prevalent sources are drainages from valley fills associated with coal mining. The ages of the fills vary. Some are of relatively recent construction and associated with active mining operations. Others are older and are no longer regulated by permits. Other sources include continuous discharge “seeps” from legacy mining operations, continuous permitted pumped or gravity flow mining discharges and drainage from fills associated with highway construction (“road fills”).

This project included a charge to provide detailed information about model inputs that are associated with NPDES permitted mining outlets. This compilation, *Mining Permitted Source Summary* provided in Appendix A and supplemented by a GIS project, includes information regarding permit responsible parties, permit and outlet status, outlet locations, associated Surface Mining Control Reclamation Act (SMCRA) permits, and outlet property ownership. With respect to older, previously permitted sources, expired permit/closed outlet information was included to the extent possible. The compilation also distinguishes mining sources between those with and without contributing valley fill areas and identifies modeled areas for both valley fill and non-valley fill land use types. It is important to recognize that elevated ion impacts from mining sources are generally associated with outlets that drain valley fills and/or those contributing pumped or gravity fed groundwater. Outlets that discharge only surface runoff from non-valley fill areas have model ion characterization that is similar to other background land uses.

Multiple source types are present in the watersheds of some impaired streams. Other, relatively smaller, watersheds are impacted by individual sources or source types. The next section describes the significant existing ion sources located the various subwatersheds of this project.

### 3.2 IONIC STRESS BIOLOGICAL IMPAIRMENTS

In the Lower Guyandotte Watershed, multiple streams have been identified by WVDEP as impaired due to nonattainment of the applicable narrative water quality criterion for biological integrity. WVDEP uses benthic macroinvertebrates to assesses biological integrity through the application of a multi-metric index (West Virginia Stream Condition Index). The WVDEP biological stressor identification process identified elevated ionic water quality as a significant stressor for a subset of those streams that are addressed in this project, as shown in [ REF\_Ref113604863 \h ].

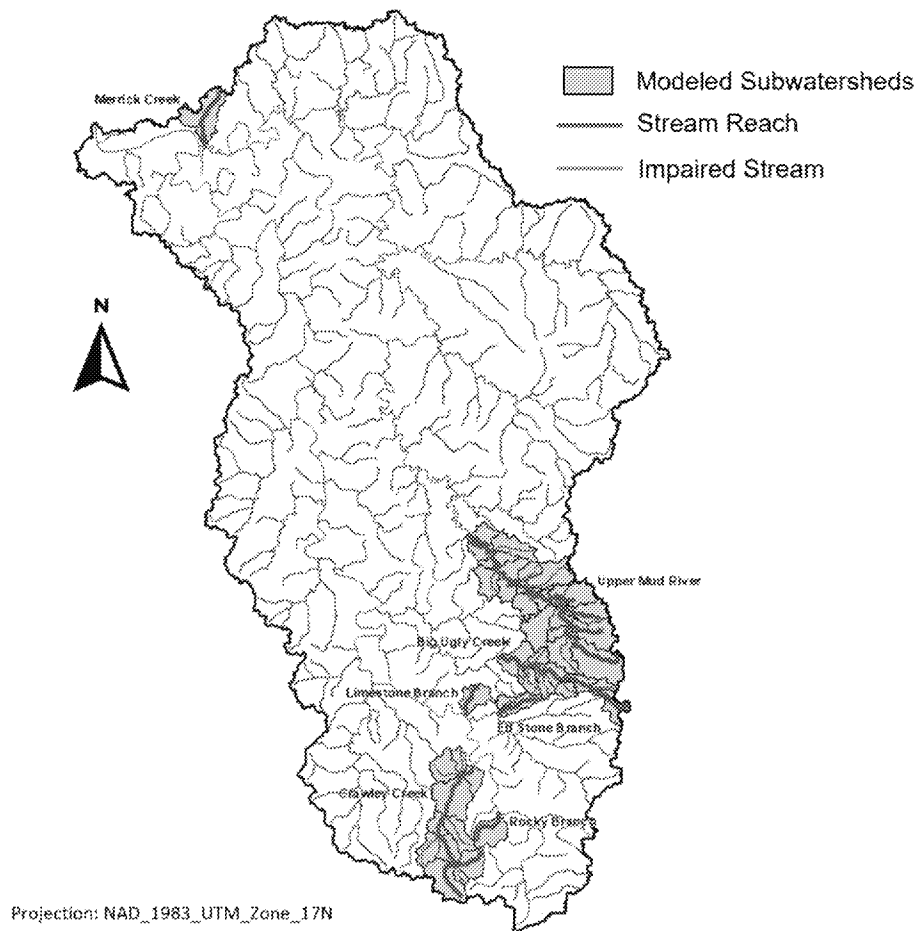


Figure [ STYLeref 1 \s ]:-[ SEQ Figure \\* ARABIC \s 1 ]. Lower Guyandotte Watershed and associated modeled subwatersheds and impaired stream reaches.

[ REF\_Ref113604367 \h ] displays the range of specific conductance values observed at monitoring locations in streams with existing elevated ion water quality. These instream values represent the contribution of sources as influenced by available dilution in their respective watersheds. Comprehensive characterization data was not available for all sources and untreated source quality will vary between sources. Particularly for observations from smaller tributary watersheds, the ionic quality of existing sources is expected to be consistent with or slightly higher than the maximum observed instream values that most often occur during seasonal low flow periods when dilution is minimized.

Table [ STYLEREf 1 \s ]-[ SEQ Table \\* ARABIC \s 1 ]. Summary of WVDEP specific conductance (SC) grab sample observations (2017-2020) at model calibration stations.

Watershed	Stream Name	NHD_ANCODE	Station ID	SUB ID	MEDIAN OBSERVED SC (uS/CM)	MAXIMUM OBSERVED SC (uS/CM)
Upper Mud River	Mud River headwaters	OGL-10	9321	445	116	223
	Lukey Fork	OGL-10-EC	13312	444	1290	2020
	Ballard Fork	OGL-10-EA	9829	442	1103	1831
	Stanley Fork	OGL-10-DX	9323	440	1305	1871
	Sugartree Branch	OGL-10-DW	9322	438	1437	1659
	Connelly Branch	OGL-10-DS	13330	436	2338	2453
	Mud River MP 74.3	OGL-10	5293	433	1116	2009
	Berry Branch	OGL-10-DN	8891	432	1792	1969
	Stonecoal Branch	OGL-10-DM	15684	430	2307	3016
	Mud River MP 71.7	OGL-10	15680	429	1684	2143
	Mud River above reservoir (MP 67.4)	OGL-10	8294	425	1336	2067
Big Ugly Creek	Big Ugly Creek MP 14.7	OGL-89	15704	658	141	286
	Big Ugly Creek MP 12.7	OGL-89	13282	654	125	233
	Fawn Hollow	OGL-89-AA	13347	653	1438	1854
	Big Ugly Creek MP 11.5	OGL-89	5107	649	250	1057
Limestone Branch	Limestone Branch	OGL-111	5144	719	360	658
Ed Stone Branch	Ed Stone Branch	OGL-112-D	5148	722	323	644
Rocky Branch	Rocky Branch	OGL-130	15637	774	600	715
Crawley Creek	South Fork/Crawley Creek	OGL-117-M	5163	765	1000	1341
	Middle Fork/Crawley Creek	OGL-117-M-1	15644	764	1330	1441
	Crawley Creek (headwater)	OGL-117	15636	766	641	964
	Crawley Creek (mouth)	OGL-117	15635	756	419	844
Merrick Creek	Merrick Creek	OGL-10-A	15606	202	436	1137

### 3.2.1 Upper Mud River

Most project impairments are associated with the Mud River mainstem and tributaries upstream of Mud River Lake ([ REF\_Ref113601134 \h ]). The mainstem segment has been identified as biologically impaired with ionic stress upstream from the reservoir to its headwaters. Practically, elevated ion water column concentrations have not been observed upstream of approximately river mile (RM) 79.5 and significant ion sources are not present in the watershed of the Mud River above that point. Identified impaired tributaries



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Sugartree Branch, Stanley Fork, and Ballard Fork enter the impaired segment of the Mud River below RM 79.5. Other tributaries with observed elevated ion concentrations also enter this segment. Those tributaries (e.g., Lukey Fork, Connelly Branch, Berry Branch, Stonecoal Branch, others) have not yet been formally identified as biologically impaired due to the lack of recent biological assessment, but nonetheless exhibit ion concentrations that must be reduced to achieve the specific conductance endpoint determined applicable to this project.

The numerous valley fills within the contributing drainage area to the impaired segment of the Mud River are the most prevalent elevated ion sources. Significant, non-valley fill/legacy mining continuous discharges are present within the Stonecoal Branch, Berry Branch, and Mullens Branch subwatersheds, and in one mainstem Mud River model subwatershed (437). One significant, permitted, continuous flow discharge of impacted groundwater is present in the Berry Branch subwatershed.

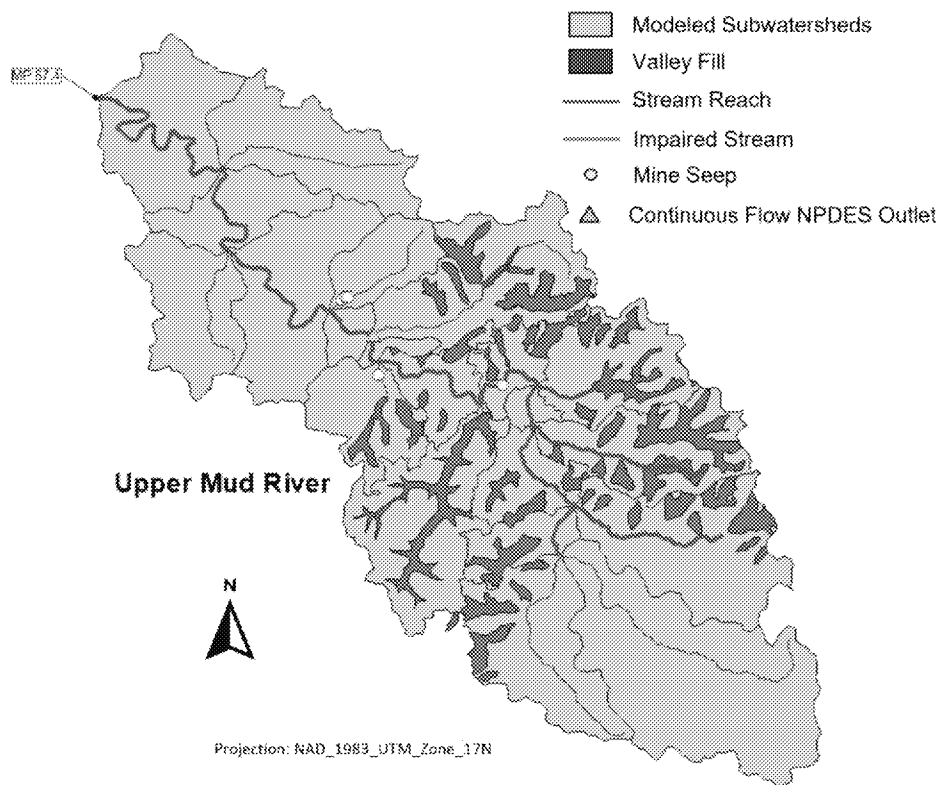


Figure [ STYLeref 1 \s ]-[ SEQ Figure \\* ARABIC \s 1 ]. Map of Upper Mud River, showing locations of valley fills and mine seeps in relation to impaired stream segments.

### 3.2.2 Big Ugly Creek

Big Ugly Creek is a tributary of the Lower Guyandotte River with the confluence located approximately four miles upstream of Ranger, WV. The mainstem segment has been identified as biologically impaired with ionic stress upstream of a location approximately 11.5 miles from its mouth (RM 11.5). In the Big Ugly watershed upstream of RM 11.5, existing elevated ion sources are limited to those located in the tributary Fawn Hollow ([ REF \_Ref113601159 \h ]). Fawn Hollow enters the impaired segment of Big Ugly Creek at approximately RM 12.7 and like Mud River tributaries Lukey Fork, Connelly Branch, etc., Fawn Hollow has not formally been identified as biologically impaired but exhibits elevated ions that must be reduced to achieve the specific conductance endpoint in Fawn Hollow and downstream Big Ugly Creek.

Non-valley fill legacy mining continuous discharges are the prevalent elevated ion sources in the Fawn Hollow watershed. A small amount of valley fill area is also present. Elevated ion sources are not present in the Big Ugly watershed upstream of the confluence of Fawn Hollow and the Fawn Hollow influence on Big Ugly Creek is abated by dilution downstream of RM 11.5.

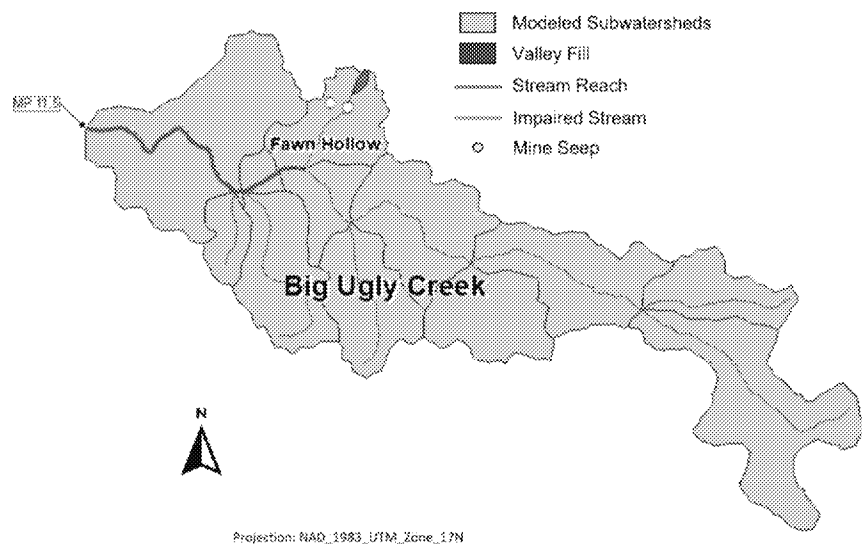


Figure [ STYLEREF 1 \s ]-[ SEQ Figure \\* ARABIC \s 1 ]. Map of Big Ugly Creek and location of Fawn Hollow, mining seeps and a valley fill in relation to the impaired stream segment.

### 3.2.3 Crawley Creek

Crawley Creek is a tributary of the Guyandotte River, with the confluence downstream near Chapmanville, WV. The entire length of the mainstem and headwater tributary South Fork have been identified as biologically impaired with ionic stress ([ REF \_Ref113601366 \h ]). The headwater tributary Middle Fork has not formally been identified as biologically impaired but exhibits elevated ions that must be reduced to achieve the specific conductance endpoint.

The most significant sources of elevated ions in the Crawley Creek watershed are discharges from valley fills and legacy mining continuous discharges located in the Middle Fork, South Fork and Crawley Creek headwater subwatersheds. Significant sources have not been identified outside of those headwater areas. The large impacts in the headwater region continue to influence ionic water quality, albeit to a somewhat lesser extent, in downstream Crawley Creek.

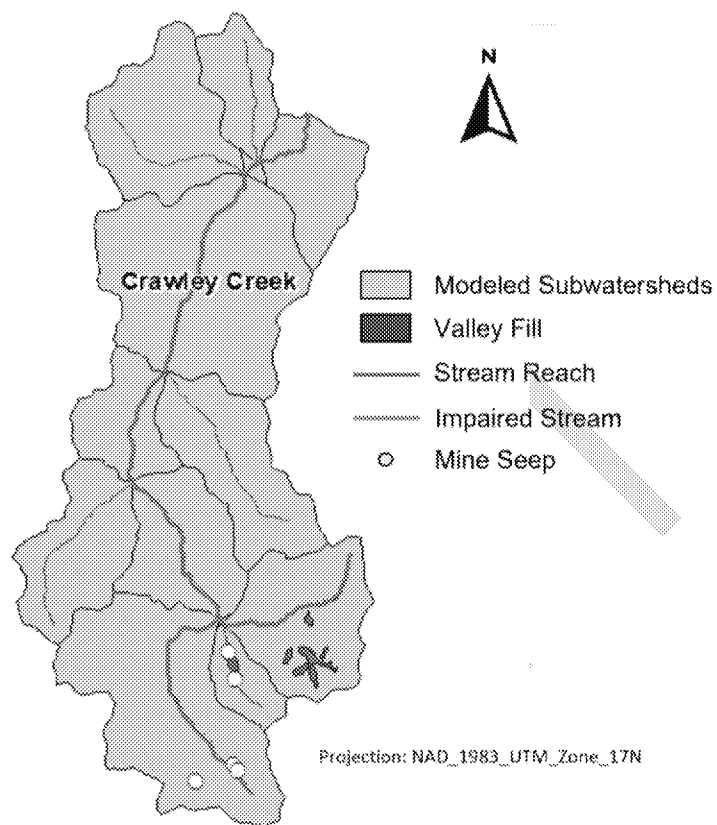


Figure [ STYLEREF 1 \s ]-[ SEQ Figure \\* ARABIC \s 1 ]. Map of Crawley Creek subwatershed and location of valley fills and mine seeps in relation to impaired stream segments.

### 3.2.4 Limestone Branch, Ed Stone Branch, Rocky Branch

Limestone Branch is a direct tributary of the Lower Guyandotte River that enters the river near Big Creek, WV. Rocky Branch is a direct tributary of the Lower Guyandotte River that enters the river between the towns of Pecks Mills, WV and Chapmanville, WV. Ed Stone Branch is a tributary of Big Creek that enters Big Creek approximately two miles upstream of its confluence with the Lower Guyandotte River at Big Creek, WV.

These small tributaries of the Lower Guyandotte River have been identified as biologically impaired with ionic stress. The only elevated ion sources identified in the watersheds of these streams are continuous flow "seeps" associated with legacy mining. The ionic strength observed near the mouth of these streams is

relatively lower than that observed in the impaired streams associated with the Mud River, Big Ugly Creek and Crawley Creek watersheds.

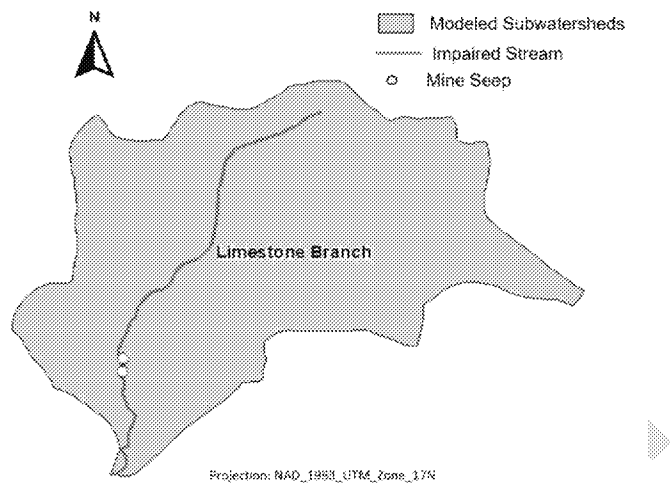


Figure [ STYLEREF 1 \s ]-[ SEQ Figure \\* ARABIC \s 1 ]. Map of Limestone Branch subwatershed and location of mine seeps in relation to the impaired stream segment.

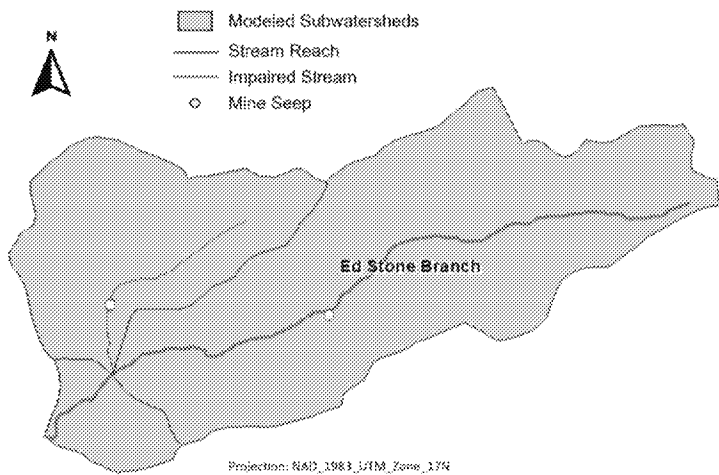


Figure [ STYLEREF 1 \s ]-[ SEQ Figure \\* ARABIC \s 1 ]. Map of Ed Stone Branch subwatershed and location of mine seeps in relation to the impaired stream segment.

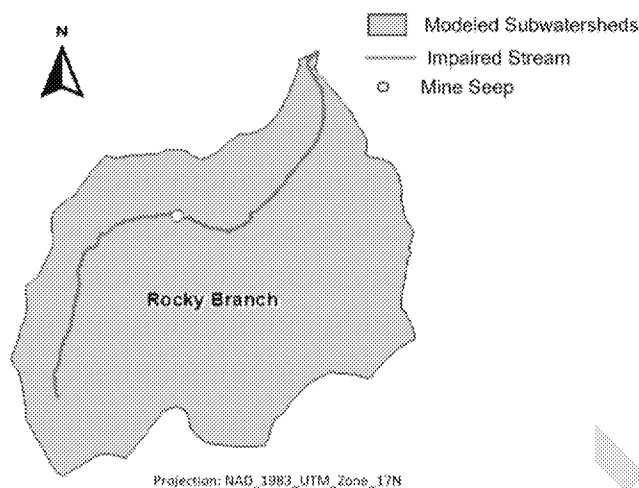


Figure [ STYLEREf 1 \s ]-[ SEQ Figure \\* ARABIC \s 1 ]. Map of Rocky Branch subwatershed and location of mine seep in relation to the impaired stream segment.

### 3.2.5 Merrick Creek

Merrick Creek is a tributary entering the Lower Guyandotte River at Barboursville, WV that has been identified as biologically impaired with ionic stress. In contrast to all other impaired streams associated with this project, no existing mining-related elevated ion sources have been identified. Valley fills associated with highway construction ("road fills") have been targeted as the sources of elevated ions. The ionic strength observed in Merrick Creek is relatively lower than that observed elsewhere, with only limited instream observations of specific conductance greater than the restoration target. The watershed of Merrick Creek is also geologically different from other areas. It is dominated by the Conemaugh geological formation wherein pockets of freshwater limestone deposits are distributed. Those deposits are present in the Merrick Creek watershed and cause streams to exhibit a naturally higher alkalinity and conductivity than those in other areas of this project (WVDEP 2022).

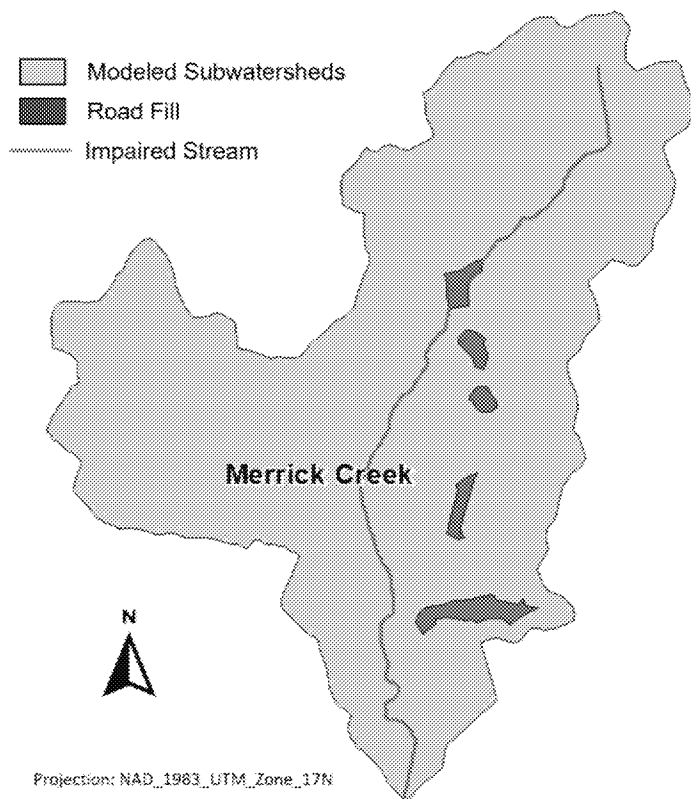


Figure [ STYLERE 1 \s ]-[ SEQ Figure \\* ARABIC \s 1 ]. Map of Merrick Creek subwatershed and location of road fills in relation to the impaired stream segment.

#### 4.0 TREATMENT TECHNOLOGY INFORMATION GATHERING

The information gathering process began with a literature search of scientific papers related to the treatment of wastewater to reduce dissolved ions. EPA Region 3 and WVDEP supplemented the initial search by providing references for potentially applicable research that were known to them. All discovered research was reviewed, and the references displayed in Appendix B were found to have relevant information about technologies that could effectively reduce ions in this setting and to discharge at levels approaching those needed to achieve the water endpoint.

Subsequently, four information gathering meetings were held. The general goals of the meetings were to identify additional effective technologies beyond those that were apparent in the literature and to capture the experience of the participants with respect to technology performance expectations and constraints. On

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November 30, 2021, a meeting was held with EPA representatives. Prior to this meeting, EPA Region 3 solicited participation from EPA representatives in other regions and headquarters with knowledge about conductivity or total dissolved solids (TDS) reduction. On December 14, 2021, a meeting was held with WVDEP TMDL, water quality assessment and mining permitting representatives. On January 26, 2022, a meeting was held with academic representatives and representatives of the U.S. Office of Surface Mining Reclamation and Enforcement (OSMRE) and the U.S. Geologic Survey (USGS). Invitations to this meeting were based upon research identified in the literature search and advice from EPA 3 and WVDEP. On January 27, 2022, a meeting was held between Tetra Tech, EPA Region 3, WVDEP, and Malcolm Mann of Saltworks, Inc. This meeting was suggested by EPA representatives as a source of information about electrodialysis reversal (EDR) technology and proved to be extremely helpful not only in that regard, but also in understanding the wastewater quality characteristics, treatment goals, and other considerations that favored EDR versus reverse osmosis (RO) and other membrane technologies.

A summary of compiled sources is provided in Appendix B. Detailed minutes of each meeting are provided in Appendix C.

## 5.0 DESCRIPTION OF TREATMENT TECHNOLOGIES

After the review of available literature and consideration of input received in the information gathering meetings, treatment technologies with potential to reduce ionic strength were assessed with respect to their ability to achieve the level of reduction necessary and relatively compared with respect to cost and operational complexity. The evaluation focused on RO, EDR, nanofiltration (NF), ettringite precipitation and bioreactor technologies. Other technologies, initially identified in the literature review with potential to reduce ions, were not evaluated further. Thermal distillation was excluded because of the extreme cost associated with vaporizing large water volumes. Ion exchange technologies do not appear capable of overall ionic strength reduction. Microfiltration and ultrafiltration technologies are not independently capable of significant ion reduction.

### 5.1 MEMBRANE TECHNOLOGIES

RO, NF and EDR are membrane technologies that are potentially available for application. Membrane technologies are the most expensive of those considered, particularly with respect to operating costs. Membrane technologies require large amounts of energy, sophisticated operation and maintenance, membrane monitoring, maintenance and replacement, and additional treatment and disposal of the concentrated brine solutions that are generated by the processes.

RO and EDR systems can be designed to reliably achieve the discharge quality determined necessary in this project, at expected flow rates. Nanofiltration can remove some dissolved solids of concern, particularly divalent ions, but is less effective in the removal of monovalent ions. As such, the ability of NF to consistently achieve the specific conductance endpoint of this project is less certain, but laboratory evaluations conducted by Kemak et al. (2018) are encouraging. They found that two of three tested nanofilters, operated at 8 bar pressure, and without pretreatment could achieve less than 500  $\mu\text{S}/\text{cm}$  in test water obtained from valley fill drainage with specific conductance ranging from 1500 -2500  $\mu\text{S}/\text{cm}$ .



RO and NF are membrane filtration technologies in which dissolved solids ions are reduced by applying pressure to move water across a semipermeable membrane that restricts the passage of ions. The solute (a.k.a., brine, reject, retentant) is retained on the pressurized side of the membrane as the solvent (a.k.a. permeate, product stream) passes through and becomes the discharge. The primary differences between RO and NF are the pore sizes of the membranes and the size of contaminants that can be removed. The pore sizes of membranes increase through common classifications of microfiltration, ultrafiltration, nanofiltration and reverse osmosis. RO membranes with smaller pore sizes can remove finer contaminants than nanofiltration membranes. However, the pressure required to move the water through NF membranes is reported to be significantly less than that required in RO. The lower pressure requirement of NF relates directly to system energy use and overall operating costs. Microfiltration and ultrafiltration via membranes or media are not effective technologies for dissolved solids removal but may be relevant pretreatment design considerations. [ REF\_Ref113895509 \h ] below illustrates a RO unit and a simple process diagram.

**Commented [AJ2]:** Do we have an estimated quantitative comparison between these? (e.g., RO can reach this level, NF can reach this level)

**Commented [AJ3]:** Similar to above, do we have a quantitative estimate of what these can achieve?

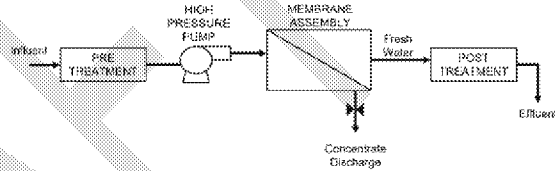
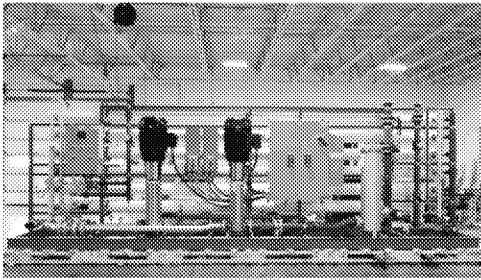


Figure [ STYLEREF 1 \s ]-[ SEQ Figure \\* ARABIC \s 1 ]. Reverse osmosis unit (Marlo, [ HYPERLINK "https://marlo-inc.com/" ]) and process diagram.

The EDR process involves applying a direct current electric field to move ions across stacked, alternating anion exchange and cation exchange membranes ([ REF\_Ref113895405 \h ]). The anion exchange membranes allow anions (negatively charged ions such as sulfate or bicarbonate) to pass through and the cation exchange membranes allow the passage of cations (positively charged ions such as calcium and magnesium). The desalted water becomes the discharge and the separated anions and cations become the

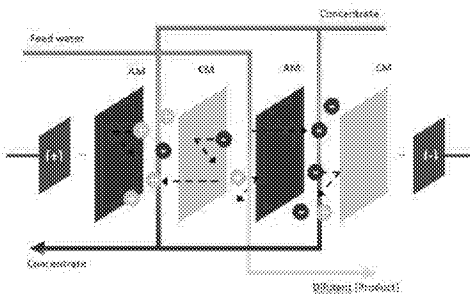


Fig.1. Schematic description of the electrodialysis reversal process

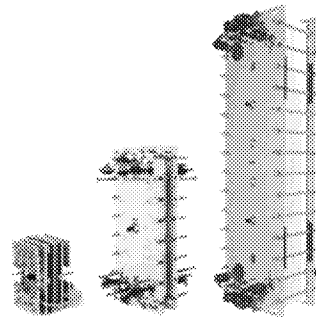


Figure 3. Three electrodialysis stacks of different sizes, showing the internal structure.

brine/reject. In contrast to the RO and NF processes that use pressure to force water through a membrane and reject the passage of ions, the EDR process moves the ions, not the water, through membranes by electricity.

Figure [ STYLEREf 1 \s ]-[ SEQ Figure \\* ARABIC \s 1 ]. EDR Process diagram (Lenntech, [ HYPERLINK "https://www.lenntech.com/" ]) and EDR units (Saltworks, [ HYPERLINK "https://www.saltworkstech.com/" ])

The relatively high proportions of brine solution generated by all membrane technologies (10-40 % of influent flow) require similar post-processing, most commonly via evaporation/crystallization or deep well injection.

Although overall costs for RO and EDR are similar, site-specific factors can economically favor one over the other. The primary considerations are the necessary change in dissolved solids concentration, the necessary dissolved solids discharge quality, and the water chemistry of the wastewater with respect to suspended solids, organics, and scaling ions. In general, RO becomes more cost effective for higher necessary TDS changes (the difference in TDS concentration between the untreated wastewater and the necessary effluent quality). EDR has been reported as more favorable if the necessary change in TDS is less than 10,000 milligrams per liter (mg/l), as is the case in this project. Conversely, EDR loses advantage as the necessary effluent quality becomes more dilute. As ionic strength in the wastewater lowers, electrical resistance increases, and relatively more energy is required to move ions. When the necessary effluent quality is 1,000 mg/l or less, the higher operating costs associated with the increased energy required by EDR may favor RO as more cost effective, despite the overall lower necessary change in TDS. EDR often gains advantages over RO because of lower wastewater pretreatment requirements. Less necessary pretreatment lowers both capitol and operation and maintenance costs. Since RO involves the pressurized impingement of ions on very small pore diameter membranes, suspended solids, organics, and scaling ions that would “blind” membranes must be removed from wastewater prior to RO treatment. Runtti et al. (2018) summarize the pre-treatment requirements for NF and RO, as shown in [ REF\_Ref113895576 \h ]. Antiscalants are commonly used in RO systems, and wastewater with higher scaling potential may require chemical pretreatment. “Not-detected” total suspended solids (TSS) concentrations have been reported as necessary for RO-friendly feeds. EDR is more tolerant to blinding because the process moves the ions, rather than water, through the membranes.

Commented [AJ4]: Aren't there examples of the brine being transported away and used for other purposes? Instead of just waste.

Feed water pre-treatment requirements for NF and RO	
Silt density index	< 5
Turbidity [NTU]	< 1
TOC [mg L <sup>-1</sup> ]	< 3
Color [APHA color units]	< 3
Metals: Fe, Mn, Al [mg L <sup>-1</sup> ]	< 0.05
Hydrogen sulfide [mg L <sup>-1</sup> ]	< 0.1
Oil and grease [mg L <sup>-1</sup> ]	< 0.1-0.5
Bacterial count [CFU mL <sup>-1</sup> ]	< 1000

Figure [ STYLEREF 1 \s ]-[ SEQ Figure \\* ARABIC \s 1 ]. General feed water pre-treatment requirements for RO and NF membranes (Runtti et al. 2018 adapted from others.)

EDR allows precise treatment to variable endpoints that may facilitate real time water quality management options. Simply, the quality of effluent is dependent upon the amount of energy applied, which can be directly controlled. In contrast, RO and NF processes are designed to constantly achieve design endpoints with little ability to adjust effluent quality.

Blending can reduce system sizes and favorably influence the overall cost of membrane technologies. Systems can be designed to highly treat a portion of the wastewater flow after which the treated flow is blended with untreated wastewater such that the total discharge achieves the necessary discharge quality. Cost savings can result from substantively reduced treatment system sizes, if reliable operation control is accomplished.

RO systems are much more common than EDR systems. RO system components have become standardized and compatible. The purchaser of an RO system will have multiple vendors from which they may obtain replacement parts. In contrast, there are limited suppliers of EDR systems and each supplier's system is specific and proprietary. As such, there has been lesser adoption of the EDR technology due to the hesitancy of potential purchasers to commit to an individual supplier.

Nanofiltration has been described as a more recent improvement of RO, which is gaining favor due to its ion removal selectivity, e.g., in potable water generation applications, its ability to remove divalent ions constituting hardness while retaining other ions that are nonproblematic and/or beneficial for human consumption. Runtti et al. (2018) concluded that nanofiltration is preferred over reverse osmosis in applications targeting sulfate removal to low concentrations due to lower operating cost. With respect to this project, NF selectivity coupled with its reduced operating cost over other membrane technologies should be considered. Due to the ability of NF to remove sulfate, calcium, and magnesium, it may be shown to be capable of consistent achievement of the specific conductance endpoint. At a minimum, its application will afford incremental improvement.

Commented [AJS]: What about EDR? The above text suggests that it is promising over RO at least. If there are major cons to EDR, please include.

## 5.2 ETTRINGITE PRECIPITATION (CESR, SAVMIN)

A commonly used method to reduce very high concentrations of sulfate in wastewater is gypsum precipitation using hydrated lime. That process cannot be expected to achieve sulfate concentrations below 1,500-2,000 mg/l due to the solubility of gypsum. Sulfate concentrations in that range are well above those that would be associated with the effluent quality needed to achieve the specific conductance endpoint of this project and may in fact be greater than concentrations of most untreated sources. As such, standalone gypsum precipitation cannot be considered as a potential practical technology.

The Cost-Effective Sulfate Removal (CESR) and SAVMIN processes are multistep processes that incorporate an ettringite precipitation stage to reduce sulfate. Ettringite precipitation is also reported to significantly reduce calcium and magnesium. An initial gypsum and metal hydroxide precipitation step may be performed first and where necessary, followed by ettringite precipitation. For wastewater with high metals content, the initial step can be further segregated to lower the generation of potentially hazardous sludge characteristics that may result from metal hydroxide precipitation. Most of the gypsum can be precipitated at a pH lower than necessary for metal hydroxide precipitation, with the remainder co-precipitated with metal hydroxides at higher pH (10.5). Ettringite precipitation occurs in the subsequent step of the process.

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Ettringite is a hydrated calcium aluminum sulfate compound that is precipitated at relatively high pH (11.3) with reactive aluminum sources (aluminum salts, aluminum-rich cements, specialized/proprietary reagents). Final pH adjustment is also necessary to neutralize the high pH generated in the treatment process, typically by recarbonation (carbon dioxide injection). The residuals generated by the process can be substantive and require dewatering and disposal. The wastes for ultimate disposal have been reported to be nonhazardous, exclusive of separated metal hydroxide sludges that may need further characterization. The reduction efficiency of sulfate has been reported to decrease with increasing magnesium ion concentration. This effect should be evaluated, but the reported half maximum inhibition concentration (54.7 mmol/L) is likely greater than expected in the untreated wastewaters of this project.

Multiple sources have reported the process capable of reducing sulfate to concentrations consistent with those that may be needed in this project (<100mg/l). Hydrometrics, Inc. advertises that the final sulfate concentrations of their CESR process are typically limited only by the amount of reagent added and the reaction time. Additionally, the process may reduce other ions in the wastewater, particularly calcium and magnesium, such that expected reductions of TDS and specific conductance are reasonable. The results of laboratory evaluations reported by Grey et al. (2018) indicated not only 85% reductions of calcium, magnesium and sulfate in test waters obtained from valley fill drainage, but also the reduction of specific conductance from the 1,500 -2,500  $\mu\text{S}/\text{cm}$  conductivity range to less than 500  $\mu\text{S}/\text{cm}$ .

Site-specific process optimization is needed to determine reagent dosing rates and reaction times. Necessary reagent dosing will depend on reagent type. Average values of proprietary reagents have been reported as 1 to 1.5 times the sulfate loading. The reaction time will depend upon the amount of reagent added, the required reduction and the presence of other ions in the wastewater. Grey et al. (2018) explored 1, 1.25, and 1.5 x sulfate load reagent dosing rates and 8, 12, and 18-hour reaction times in experiments with valley fill drainage test waters and determined a dosing rate of 1.25x sulfate load with reaction time equal to 18 hours to be optimal. Process optimization must also consider the aluminum residual with respect to final effluent quality. Although all added treatment chemicals can be theoretically precipitated, suboptimal operation may result in elevated aluminum in the treated effluent.

Capital costs for an ettringite precipitation process are likely to be much lower than those associated with the various membrane technologies previously discussed. A significant economic advantage of ettringite precipitation over membranes is lower operating costs due to low energy demand. Additionally, the process does not generate the liquid brine waste streams that are commonly associated with the membrane technologies, and which require additional sophisticated and expensive treatment and disposal. Dewatering of residuals can be accomplished with more conventional dewatering equipment (filter or belt press). According to Hydrometrics, Inc., operating costs are reported to be dominated by reagent cost. They report their proprietary reagent costs at \$0.40/pound, as well as a reagent cost of \$3/1,000 gallons treated, for a 1,500 mg/l sulfate reduction. Residual disposal is an additional, likely non-negligible operating cost consideration.

### 5.3 BIOREACTORS

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Bioreactors (a.k.a. biochemical reactor, [BCRs]) use microorganisms to reduce pollutants in wastewaters associated with both coal and hard rock mining operations in the United States and abroad. Most past applications targeted acid mine drainage and were designed for acidity and metals reduction. More

recently, bioreactors have been optimized for sulfate reduction and some have been designed for selenium removal. Bioreactors are attractive because they have historically been demonstrated as a low cost, low maintenance, low energy alternative to active treatment systems at mine sites. However, most existing biological systems have not been specifically designed to reduce ionic strength in terms of TDS or conductivity and their ability to achieve the level of reduction necessary in this project is unproven. Nonetheless, the limited available research indicates that modest ionic strength reductions are possible with this technology.

Various designs of bioreactors include ponds, tanks, trenches, and wetlands. Systems can operate passively or actively. Passive bioreactors use a simple flow through design with a solid reactive mixture acting as a source of nutrients for the bacteria and as a substrate for microbial attachment and metal sulfide precipitation. The substrate is intended to support sulfate reducing bacteria for a fixed period after which system rehabilitation is required. Active systems may include continuous external sources of the organic substrate and/or separate tanks or zones for the biological, chemical, and physical processes.

[ REF\_Ref113895604 \h ] displays multiple pathways by which bioreactors may reduce conductivity. Bioreactors at mine sites include an anaerobic zone where sulfate-reducing bacteria accomplish the sulfate reduction that is the expected to be the primary mechanism enabling overall ionic strength reduction.

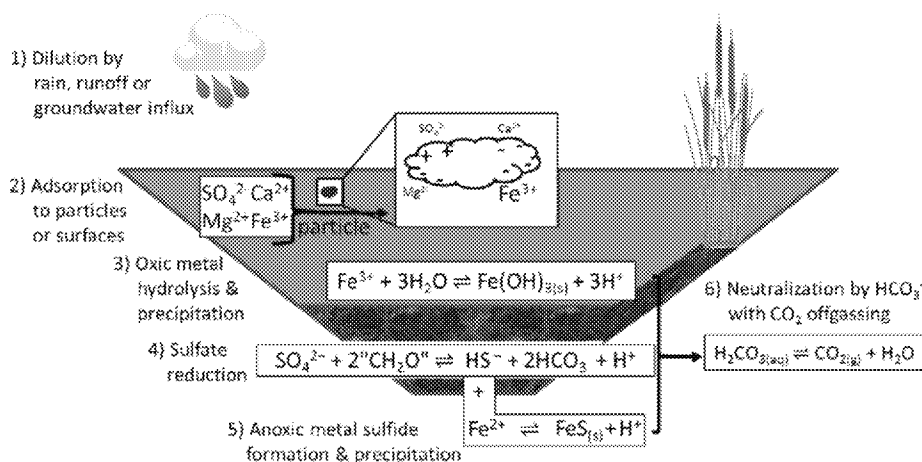


Figure [ STYLEREF 1 \s ]-[ SEQ Figure \\* ARABIC \s 1 ]. Primary processes to reduce conductivity in a bioreactor system (Smyntek et al. 2017).

Systems designed primarily for AMD abatement employ limestone substrates in bioreactors and/or introduce other alkalinity sources. As such, and with respect to TDS performance, the reduction of sulfates accomplished may be counteracted not only by the alkalinity generated in the reaction, but also by alkalinity added through dissolution of limestone. Lefticariu et al. (2015) indicates that anaerobic organic substrates in bioreactors do better at sulfate reduction than bioreactors with limestone substrates. The exclusion of limestone may be entirely suitable for the alkaline or circumneutral wastewaters associated

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with this project if alternative substrates such as nonreactive gravel can provide the necessary structural stability.

When compared to the other technologies discussed in the report, biological systems are expected to be significantly less expensive in terms of capital cost, operating cost, and complexity. Significantly less energy and material inputs are also expected. Although still less costly and operationally intensive than other technologies, active bioreactors are expected to have higher capital and operating costs when compared to passive bioreactors. Land requirements may be significant for systems or components involving ponds or wetlands. Extensive maintenance is not needed for passive systems, but performance can decline over time due to the exhaustion of the initial microbial nutrient source and/or substrate clogging and require complete reactor rehabilitation. Initial sulfate reduction performance in bioreactors may be poor because time is needed for optimum microbe development. The addition of a bacteria inoculum at start-up may lessen the system lag time to achieve maximum performance. Bioreactors have successfully operated in cold climates, but seasonal performance variation may be expected. As with most biological processes, performance is expected to be better in warmer months.

Best-case expected conductivity reductions of 30 - 40% were anecdotally indicated by multiple experts/practitioners in the information gathering meetings. The literature review of passive biological treatment systems presented in Smyntek et al. (2017) ([ REF\_Ref113895627 \h ]) supports that maximum range, states that the maximum predicted conductivity change is approximately equal to the maximum change by stoichiometry for sulfate reduction, and qualifies that maximum performance can be expected only from limestone-free systems. All reviewed systems with limestone increased conductivity, but 22 of 25 limestone-free systems reported conductivity reductions.

Reference	No.	Region	Treatment type	Influent	Effluent	Change
				$\mu\text{S cm}^{-1}$		%
Fyson et al., 1998	1	Germany	Laboratory-scale VFB†	1600	1300	-19%
Kapler et al., 1999	2	West Virginia & Pennsylvania	Field-scale VFB	1000-3400	930-2550	-38 to +30
Fyson et al., 2006	3	Germany	Laboratory-scale VFB	1033	576	-44%
Pehler et al., 2007	4	Colorado	Field-scale VFB	3430-5760	3350-5560	-18 to +10
Blumenstein et al., 2008	5	California	Laboratory-scale VFB	2900	3700-4700	28 to 62
Gusek et al., 2008	6	California	Field-scale VFB	1453	1027	-29
Blumenstein and Gusek, 2009	7	California	Field-scale VFB	3000	3000	0
Kumar et al., 2011	8	Australia	Laboratory-scale VFB	11000	10700	-3%
Kumar et al., 2011	8	Australia	Laboratory-scale VFB	10800	7100	-34%
Gandy and Jarvis, 2012	9	England	Laboratory-scale VFB	580	615	6
Gandy and Jarvis, 2012	9	England	Field-scale VFB	580	604	4
Song et al., 2012	10	South Korea	Field-scale VFB	2400	2500	4
Santamaria, 2014	11	Oklahoma	Laboratory-scale VFB	1200-1320	1150-1550	-10 to +20
Yim et al., 2015	12	South Korea	Field-scale VFB	2000	2000	0%
Manzillo et al., unpublished data, 2015	13	Pennsylvania	Laboratory-scale VFB	863	635	-26%
Tarutis and Uex, 1990	14	Pennsylvania	Constructed wetlands	711	592	-17
Wildeman et al., 1993	15	Colorado	Constructed wetlands	8000-10830	9240-12200	-6 to 44
Stark et al., 1994	16	Ohio	Constructed wetlands	1790	1702	-5
Sikora et al., 1996	17	Alabama	Constructed wetlands	1120	1230-1270	9.8 to 13
Heil and Kerins, 1988	18	Montana	Constructed wetlands	3349	3440	3
Heil and Kerins, 1988	18	Montana	Constructed wetlands	2414	2559	6
Skousen et al., 1999	19	West Virginia	Constructed wetland & anoxic limestone drain	900	880-1400	-2 to +56
Skousen et al., 1999	19	West Virginia	Constructed wetland & anoxic limestone drain	4700	1200-4500	-47 to -4
Hilton et al., 2003	20	Pennsylvania	VFB & constructed wetland	1880	1750	-6%
Hilton et al., 2003	20	Pennsylvania	VFB & constructed wetland	1432	1335	-7%
Hilton et al., 2003	20	Pennsylvania	VFB & constructed wetland	1140	939	-18%
Rose et al., 2004	21	Pennsylvania	VFB & constructed wetland	1100-3210	990-3210	-18 to +23
Shenoi, 2005	22	India	Natural wetland	7240-8153	7082-5674	-15 to -30%
Behum et al., 2006	23	Oklahoma	Constructed wetland	480	500	4
Shenoi, 2006	24	India	Laboratory-scale constructed wetland system	1520-1590	737-1810	-52 to +14%
Cravotta, 2007	25	Pennsylvania	Oxidation pond & constructed wetlands	517	513	-1%
Eger, 2007	26	Minnesota	Natural wetland	1100	600	-45%
Hedin, 2013	27	Pennsylvania	Oxidation pond & constructed wetlands	2688	2434	-9%
Cravotta and Brady, 2015	28	Pennsylvania	Constructed wetland	504	477	-5%
Cravotta and Brady, 2015	28	Pennsylvania	Constructed wetland	2040	2030	0%
Cravotta and Brady, 2015	28	Pennsylvania	Constructed wetland	1510	1390	-8%
Cravotta and Brady, 2015	28	Pennsylvania	Constructed wetland	865	590	-32%
Cravotta and Brady, 2015	28	Pennsylvania	Constructed wetland	2600	2570	-1%
Cravotta and Brady, 2015	28	Pennsylvania	Oxidation pond & constructed wetlands	650	606	7%
Cravotta and Brady, 2015	28	Pennsylvania	Constructed wetland	1980	1930	-3%
Cravotta and Brady, 2015	28	Pennsylvania	Constructed wetland	2100	1920	-9%
Cravotta and Brady, 2015	28	Pennsylvania	Constructed wetland	992	1080	9%

† VFB, vertical flow bioreactor.

‡ The treatment did not include limestone.

Figure [ STYLEREFF 1 \s ]-[ SEQ Figure \\* ARABIC \s 1 ]. Changes in conductivity following passive biological treatment of mine drainage impacted waters (Smyntek et al. 2017)

During the academia/OSMRE information gathering meeting, participants suggested the TDS/conductivity reduction performance of bioreactors designed for selenium removal may differ from that associated with bioreactors designed for pH increase and metals removal. Selenium impacts have been mostly associated with net alkaline drainage scenarios, and minimization of alkalinity additions or avoiding the use of limestone components might suggest improved sulfate performance. But systems in which microorganisms

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are optimized for selenium reduction may accomplish lower sulfate reduction. Unfortunately, no data has been made available for selenium bioreactors to assess their conductivity or TDS reduction performance.

In summary, it is unlikely that bioreactors will ever be able to fully and consistently achieve the ionic reduction needed for sources in this project. At this time, bioreactors may be practical to reduce TDS/conductivity in lower strength waste streams, could be applied as an incremental improvement option for legacy mining impacts, or be used as pretreatment or polishing components of a treatment train. Those limited benefits may be expanded with continued research aimed at optimizing conductivity reduction performance.

#### 5.4 NON-TREATMENT MANAGEMENT CONTROLS

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Although conceptually feasible, little information was identified that demonstrated the practicality of non-treatment management controls to resolve or reduce ionic loading impacts. Nonetheless, it is reasonable to expect that discharge minimization, effluent holding, and blending with a dilution source, applied independently or in combination, could positively impact the ionic water quality conditions. Real time water quality management scenarios have been pursued elsewhere where discharges can be controlled to maintain instream targets during the critical low-flow condition that is present in this project.

Merriam et al. (2020) demonstrates a practical approach to maintain a 500 mg/L TDS target in the Monongahela River via control of discharge volume from pumped sources and flow augmentation from reservoirs during critical low flow conditions. That approach may be replicated in scenarios where assimilative capacity exists, or is made available, in the management waterbody and high concentration ionic inputs can be modulated. Neither prerequisite appears available to the sources and small receiving stream impairments of this project, but similar concepts could be explored, particularly with respect to potential incremental water quality improvement.

As examples, the spray back of effluent to vegetated areas during summer months, and the associated reduction of effluent discharge volumes through evaporation and transpiration, could be evaluated. The practicality of holding effluent or controlling the discharge rate in relation to receiving stream flow during critical stream flow conditions could be assessed. Additionally, the development of a dilution water source and holding could be considered to enable blending (and lowering the ionic strength) of the discharge during critical periods.

Real time water quality management is not envisioned as a panacea. Successful approaches might involve:

- Site-specific feasibility evaluations to identify potentially available control mechanisms
- Construction of holding basins
- Dedicated onsite operators
- Receiving stream and effluent flow measurement capability
- Effluent and receiving stream monitoring
- Coordination with control authorities to develop thresholds to trigger controls and other implementation requirements

It is expected that reducing valley fill inflow would lower both the opportunity for reaction with spoil materials and the outflow volume. Many new fill construction best practices to minimize water influx could not be practically implemented at existing fills but there may be limited opportunities to retrofit adverse



surface conditions and lower water influx. Incremental actions that lower effluent discharge during the critical period or create or supplement a dilution source will ease constraints for holding or blending activities.

Also note that the biological condition in the immediate receiving stream for an instream outlet would not substantively improve by simply reducing the volume of a high ionic strength discharge volume because stream biota would continue to be subjected to similar water quality characteristics. Less water at the same ion quality would likely have same biological impact. But in incremental improvement pursuits targeting a downstream segment with limited assimilative capacity, standalone volume control at upstream sources could be a positive influence.

## 5.5 NEW VALLEY FILL DESIGN CONSIDERATIONS

The publications reviewed in this section address new valley fill design considerations and construction techniques to minimize dissolved solids export. Recommended approaches may not be practical for retrofit applications to existing valley fill sources but should be considered if new mining operations involving valley fills are proposed within the watersheds of the impaired streams associated with this project, or elsewhere.

Identified best practices are based upon the general principles of minimizing the amount of water entering the fill and minimizing water contact and contact time with spoil materials within the fill that have the highest potential to generate dissolved solids. The recommended set of practices are intended to lower the export of dissolved solids from the mining operation, create site hydrology that mimics pre-mining hydrology, and expedite the return of the site to a forested ecosystem.

The following TDS export reduction practices have been identified in the literature:

- Systematically characterizing the conductivity generating potential of all spoil subtypes before mining;
- Planning construction (backfill and valley fill) to maximize the placement of lower conductivity generation potential materials in flow path areas and encapsulating the highest conductivity generation potential materials to minimize their contact with water ([ REF \_Ref113895652 \h ]).  
More specifically,
  - Constructing valley fill underdrains with low reactivity, large, durable rock
  - Selecting weathered overburden (generally spoil from the upper 10-25 feet) for flow path areas because it is less reactive than more deeply located “unweathered spoil” after exposure
  - Avoiding placement of higher conductivity generation potential spoils near sides or bottom
  - Isolating and encapsulating the highest conductivity generation potential spoil (shales, pyritic material);
- Constructing fills by “bottom-up, truck and place” methods and not by “end dump” methods that comingle spoils of variable conductivity generation potentials;
- Providing in-situ filters atop valley fill underdrains to minimize passage of fine materials, which have higher unit surface area and produce more conductivity than larger particles;
- Minimizing the amount of spoil material to be disposed of in valley fills by higher stacking and/or use in constructing weep berms, thereby lessening the length of stream overlain by the valley fill;

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- Preventing extraneous groundwater entry to fills by intercepting and daylighting sources along low conductivity generating pathways;
- Minimizing the infiltration of precipitation into the fill, generally, and especially to deeper regions of the fill where bulk fill materials of moderate conductivity generation potential are located. More specifically,
  - Use of weep berm technology for solids retention and supernatant dispersal to off-fill forested areas to rather than routing to on bench ponds or settling basins
  - Use of the Forestry Reclamation Approach (FRA) and its loose dumped spoil final cover provision to create a surface amenable to tree growth and minimize water entry to bulk fill
  - Avoiding the creation of areas of standing water on the fill
  - Lining ditches atop the fill or pitching them to quickly direct flow off the fill
  - Minimizing flat areas.

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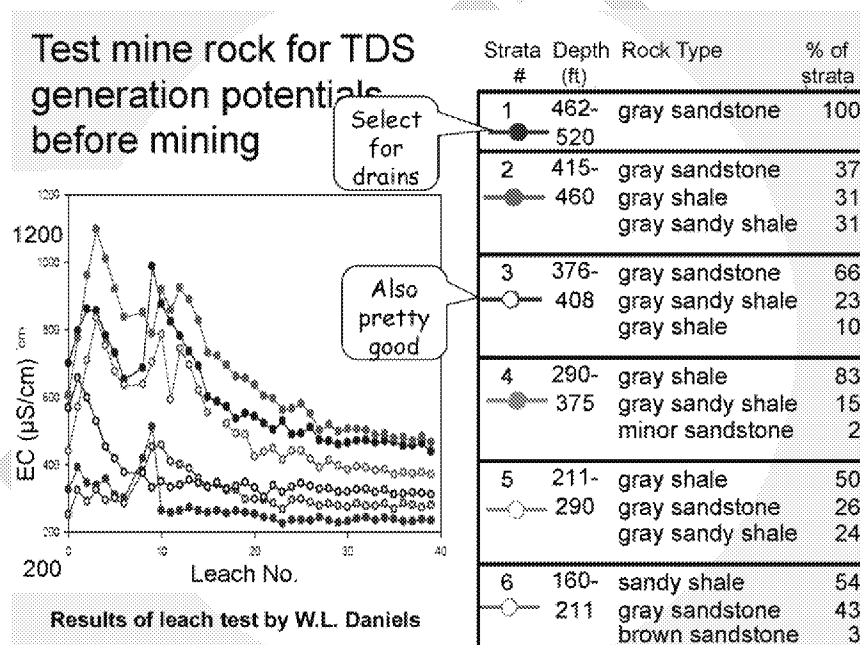


Figure [ STYLERE 1 \s ]-[ SEQ Figure \\* ARABIC \s 1 ]. Results of mine rock conductivity and which strata are most appropriate for placement in the flow path (Zipper et al. 2016).

## 5.6 CENTRALIZED TREATMENT

Significant ion sources are concentrated in some parts of the Lower Guyandotte project area, and the feasibility of centralized treatment for geographically proximate sources could be explored to achieve economy of scale and mitigate constraints that hinder source-specific control (e.g., access, availability of electricity, usable land for treatment systems or other controls).

Conceptually, multiple sources could be routed to a strategic location for treatment that is minimally constrained via a transport system of pipes with gravity or pumped flow. The fate of the treated water (discharge at treatment location, return to original source location, hybrid) would be determined by consultation with the control authority as the seasonal biologically-necessary stream flow conditions of various segments must be considered.

Centralized treatment is not likely to be the solution to all project impairments but, like non-treatment controls, may afford opportunities to address some impaired streams and/or achieve incremental improvement in others.

## 6.0 SUMMARY AND RECOMMENDATIONS

[ REF\_Ref113621888 \h \\* MERGEFORMAT ] provides a relative comparison of key considerations for potential ion reduction treatment technologies. As is clear, the known technologies that can reliably achieve the necessary reduction performance are simultaneously the most expensive, complex and energy demanding. Conversely, the least-expensive, simplest, and non-energy demanding biological technologies are not likely to be independently capable of substantive ion reduction.

Table [ STYLEREF 1 \s ]-[ SEQ Table \\* ARABIC \s 1 ]. Comparison table summarizing key considerations of various treatment technologies.

Technology	Cost	Ion reduction performance	Residual Generation	Operational Complexity	Energy Demand
Reverse Osmosis	\$\$\$	+++	+++	+++	+++
Electrodialysis Reversal	\$\$\$	+++	+++	+++	+++
Nanofiltration	\$\$	++	+++	++	++
CESR	\$	++	++	++	+
Biological Reactors	\$	+	+	+	-

Consideration should be given to the cost and performance reliability tradeoffs associated with nanofiltration and CESR technologies. Although there is less available research for them, that which was reviewed indicates that both can be designed and operated to reduce mining wastewater of untreated ion quality consistent with the existing sources for this project to 500  $\mu\text{S}/\text{cm}$  specific conductance.

The general and relative information presented herein can be used only as a starting point. Ideally, feasibility evaluations should be conducted at sites, or groups of sites, to evaluate the potential treatment and management controls or combinations thereof that may be locally practical. Scenarios could be evaluated not only with respect to achieving final targets at individual sites, but also to precisely identify the cost and expected performance of various alternatives or combinations to inform the pursuit of incremental improvement. Associated with incremental improvement, local feasibility studies could also include evaluations of the potential controls for multiple sites wherein the feasibility of combined treatment may be explored, and subsets of the most impacting sites could be evaluated with respect to the

environmental benefits that would be expected in a downstream water segment that is influenced by the group.

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## APPENDIX A: MINING PERMITTED SOURCE SUMMARY

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## APPENDIX B: COMPILED TREATMENT TECHNOLOGY RESOURCES

(To be updated)

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## APPENDIX C: MEETING MINUTES

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